# PROCESSING OF CARBON REINFORCED THERMOPLASTIC COMPOSITES

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## ABSTRACT

The aim of this work is to produce and optimize the processing of carbon fibres thermoplastic matrix pre-impregnated materials (towpregs and PCT´s) using the dry powder coating equipment from our own laboratories. Pultrusion was the selected manufacturing method for processing all carbon fibres thermoplastic matrix pre-impregnated materials into composite parts.

The optimization of the pultrusion processe was made by studying the influence of the most relevant processing parameters in the final properties of the produced carbon fibres thermoplastic matrix pre-impregnated materials and composites.

The composite relevant mechanical properties were determined and studied. The final composites were also submitted to Scanning Electron Microscopy (SEM), optical microscopy and calcination tests.

The determination of the fiber volume fraction of a composite with a high melting temperature thermoplastic polymer used as matrix was obtained comparing the results of thermogravimetric analysis (TGA) with the calcination tests.

## 1. Introduction

Composites with thermoplastic matrices offer increased fracture toughness, higher damage tolerance, short processing cycle times and excellent environmental stability. They are recyclable, post-formable and can be joined by welding. The use of long/continuous fibre reinforced thermoplastic matrix composites involves, however, great technological and scientific challenges since thermoplastics present much higher viscosity than thermosettings, which makes much difficult and complex the impregnation of reinforcements and consolidation tasks [1-4].

Today, two major technologies are being used to allow wet reinforcing fibres with thermoplastic polymers [1-2]: i) the direct melting of the polymer and, ii) the intimate fibre/matrix contact prior to final composite fabrication. Continuous fibre reinforced thermoplastic matrix pre-impregnated tapes (PCT´s) are, for example, produced by direct melting processes. Alternatively, intimate contact processes allow producing cheap and promising pre-impregnated materials, such as, commingled fibres and powder coated towpregs.

Pultrusion was the selected manufacturing method for processing all these pre-impregnated materials into composite parts. It is a versatile continuous high speed production technology, allowing the production of fibre reinforced complex profiles. The optimization of the pultrusion process was made by studying the influence of the most relevant processing parameters in the final properties of the produced pre-impregnated materials and composites [5-10]. The method of Taguchi/DOE (Design of Experiments) was used to achieve this aim.

The possibility of using maleic anhydride as compatibilizer of carbon and glass fibre reinforced polypropylene composites was also analysed in the present work.

The final composite parts were also submitted to tensile, interlaminar and flexural tests, as well as calcination and optical microscopy, SEM and TGA tests and the results were compared with theoretical ones that can be predicted by using the ROM (Rule Of Mixtures).

## 2. Experimental

### 2.1. Raw Materials

The following raw materials were used to produce CF/PP pre-impregnated materials for this work: i) a PP powder ICORENE 9184B P® and carbon fibre roving M30 SC® from the ICO Polymers and TORAY, respectively, were used to produce the CF/PP towpregs, ii) PP powder Moplen RP348U® from Basell and the carbon fibre roving already mentioned were used to manufacture the CF/PP PCT tapes. On other hand, composite parts for highly demanding advanced markets were processed from towpregs manufactured by using a highly aromatic amorphous thermoplastic polymer in powder form, the Primospire® PR 120 from Solvay Advanced Polymers, and 760 Tex M30SC carbon fibre tows TORAY.

Tables 1 and 2 summarise relevant properties of the polypropylene, Primospire® and carbon fibres used in present work to produce pre-impregnated raw materials (towpregs and PCT´s).

| **Property** | **PP powder** (ICORENE 9184B P®) | | **Primospire®** | | **PP granules** (Moplen RP348U ®) |
|---|---|---|---|---|---|
| | Manufacturer datasheet | Experimental | Manufacturer datasheet | Experimental | Manufacturer datasheet |
| Specific gravity ($Mg/m^3$) | 0.91 | 0.91 | 1.21 | - | 0.90 |
| Tensile strength (MPa) | Yield Strength 30 | Yield Strength 19 | 207 | 104 | Yield Strength 30 |
| Young Modulus (GPa) | 1.3 | 0.98 | 8.3 | 8.0 | 1.1 |
| Poisson´s ratio | - | 0.21 | - | | - |
| Average powder particle size (µm) | 440 | 163 | - | 139 | - |
| Glass transition temperature ($T_g$) | Typical value 0-20 | - | 158 | 156 | Typical value 0-20 |
| Melting temperature ($T_m$) | Typical value 170 | 166 | - | - | Typical value 170 |

Table 1. Properties of Towpregs and PCT powders raw-materials

| **Property** | **Carbon fibre** (TORAY M30 SC®) | |
|---|---|---|
| | Manufacturer datasheet | Experimental |
| Linear density (Tex) | 760 | - |
| Specific gravity ($Mg/m^3$) | 1.73 | - |
| Tensile strength (MPa) | 5490 | 2731 |
| Young Modulus (GPa) | 294 | 194.5 |
| Average fibre diameter | 5 | 7.37 |

Table 2. Properties of Towpregs and PCT fibre raw-materials

### 2.2 Production of Thermoplastic Matrix Pre-Impregnated Products

The dry powder coating equipment used to produce fibre reinforced towpregs is schematically depicted in Figure 1 [7-10].

The pre-consolidated tapes (PCT´s) used in this work were produced in a cross-head extrusion equipment (see Figure 2) from our own laboratories [10].

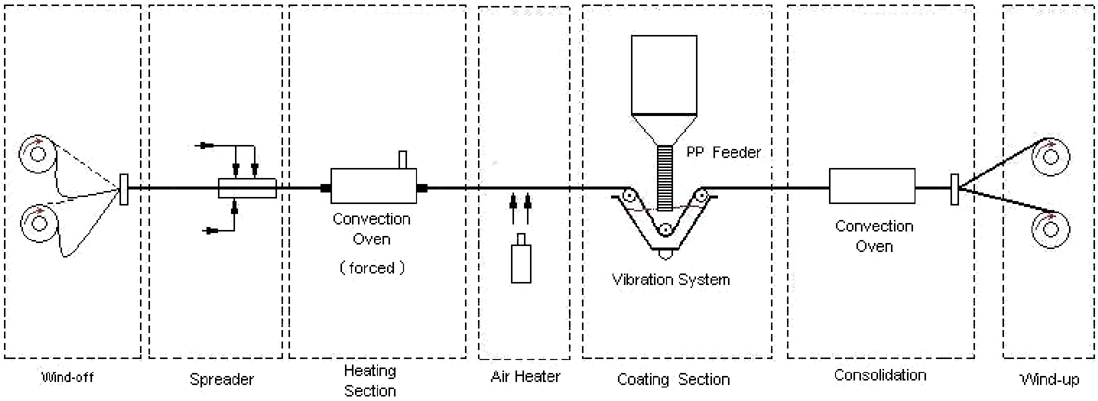


Figure 1. Powder coating line setup

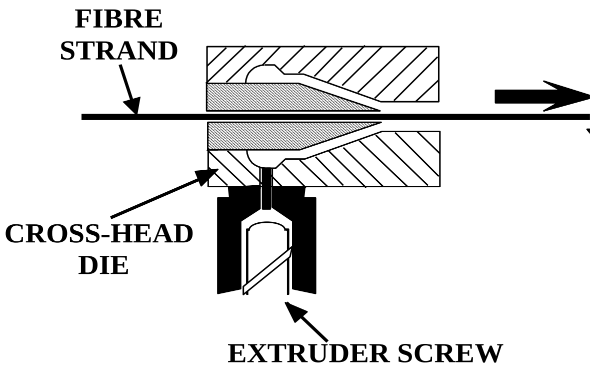


Figure 2. Cross-head extrusion die

**2.2.1. CF/PP and CF/Primospire® towpregs production**

In order to optimize the production of CF/PP powder coated towpregs, different processing variables combinations were experimented and the number of trials optimized using the Taguchi approach. The studied operational parameters were:

- heating oven temperature (600, 650 and 700 ºC); consolidation oven temperature (350, 400 and 450 ºC); linear pull speed (4, 6 and 8 m/min).

The Taguchi approach was applied to the towpregs production process in order to obtain the condition that maximizes polymer powder content.

The polymer mass fraction in the towpregs was determined by weighting towpreg strips produced in those different conditions.

The optimal condition obtained from Taguchi method application led to the following operating parameters selection: heating oven temperature and consolidation oven temperatures of 700 ºC and 400ºC respectively, and a linear pulling speed of 6 m/min. Using this optimal operative condition, the amount of polymer should increase up to 45.6%. However, it was found that the average polymer content in continuous towpreg production was only 40.0%.

In order to produce CF/Primospire® towpregs, the powder coating equipment was operated at different following woven temperatures and fibre linear pull speeds:

- heating oven temperature (700 ºC); consolidation oven temperature (500 - 550 ºC); linear pull speed (4 and 6 m/min). From such work the best values of the operational variables, which allow simultaneously producing towpregs in good and stable circumstances and having the maximum polymer powder content were:

- heating oven temperature - 700 ºC; consolidation oven temperature - 525 ºC and linear pull speed - 6 m/min. Using those conditions towpregs with a polymer mass content of approx. 40% were produced.

### 2.3 Pultrusion of pre-impregnated materials

The towpregs and PCT’s were processed into composite bar profiles using the laboratorial pultrusion line, Figure 3 [7-10].

To produce composite profiles, the pre-impregnated materials are guided into the pre-heating furnace to be heated up to the required temperature. Then, they enter in the pultrusion heated die to be heated and consolidated to the required size and, after cooled down in the cooling die to solidify.

In this work, it was designed and manufactured a die to allow producing a 20×2 mm2 bar-shaped profile.

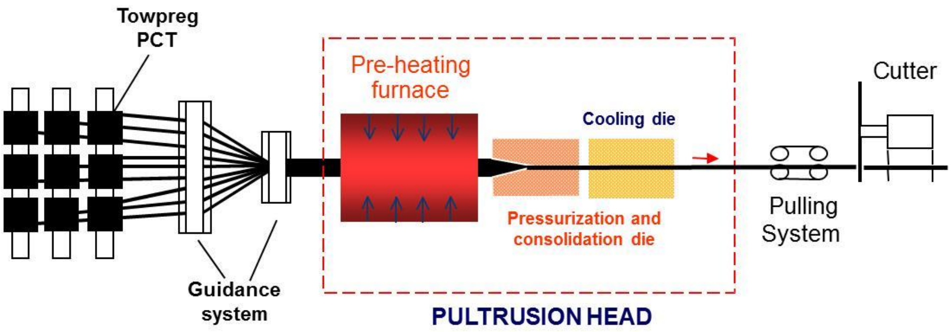


Figure 3. Schematic diagram of the pultrusion line

Those profiles were manufactured from different pre-impregnated materials, using operating conditions in order to optimize the processing.

#### 2.3.1 Towpreg processing

CF/PP towpregs were manufactured by pultrusion into composite bar profiles using the most relevant operating conditions. The Taguchi´s/DOE method was applied, maintaining the cooling die at 25 ºC, in order to optimize the processing parameters:

i) furnace temperature (160 or180 ºC); ii) heating die temperature (240 or 260 ºC); iii) linear pull-speed (0.2 or 0.3 m/min).

Results have shown that was not possible to produce, in steady, conditions pultruded profiles from towpregs at pultrusion speeds and consolidation die temperatures higher than 0.4 m/min and 260 ºC, respectively. By using higher values of these two parameters, the process became unsteady, mainly due to reflux and accumulation of the thermoplastic polymer at the entrances of the consolidation and cooling dies.

The found optimal operating conditions that maximize mechanical properties were: furnace and heated die oven temperatures of 160 ºC and 260ºC respectively, and a linear pulling speed of 0.2 m/min.

The CF/Primospire® pultruded bars were produced in this work with the following operational conditions: i) furnace temperature (380 - 400 ºC); ii) heating die temperature (420 - 475 ºC); iii) linear pull-speed of 0.2 m/min.

#### 2.3.2 Pre-consolidate tapes (PCT´s) processing

PCT´s were processed into rectangular 20×2 (mm2) bar using the already mentioned pultrusion equipment being operating conditions shown in Table 3.

| Raw-material | Heated die temperature (ºC) | Cooled die temperature (ºC) | Furnace temperature (ºC) | Pulling speed (m/min) |
|---|---|---|---|---|
| CF/PP PCT | 230 | 50 | 160 | 0.2 |

Table 3. Pultrusion processing parameters for PCT´s

## 2.4 Testing

### 2.4.1 Microscopy analysis

To determine the impregnation quality and to evaluate the fibre distribution and fibre/matrix adhesion of the thermoplastic composites, their cross-sections were studied under optical microscopy (CF/PP) and under by SEM-scanning electron microscopy (CF/Primospire®).

### 2.4.2 Mechanical testing

Bar samples were submitted to flexural, tensile and interlaminar testing according to the ISO standards 14125, 527 and 14130, respectively.

The mechanical properties were compared to the theoretical ones predicted by using the Rule of Mixtures (ROM).

Tensile tests were conducted, according to ISO 527, in a 100 kN universal testing machine at the crosshead speed of 2 mm/min using 180×20×2 $mm^3$ rectangular samples obtained from pultrusion.

The tensile modulus was determined from the slope of the initial linear portion of the experimental stress/strain curve. A SG Shimadzu® 50 mm length strain-gauge was used up to 0.3% strain, for accurate determination of the tensile modulus.

Three-point flexural tests were also conducted on five 100 × 20 × 2 $mm^3$ pultruded profiles specimens and 100 × 15 × 4 $mm^3$ for the compression moulded samples, using 100 kN universal testing machine and a distance between supports of 80 mm, according to ISO 14125, at a crosshead speed of 1 mm/min.

Samples with dimensions of 20 × 20 × 2 (mm3), cut from composites processed from each pre-impregnated raw material, were submitted to interlaminar shear tests according to ISO 14130. The tests were conducted in a 50 kN universal testing machine by using an initial pre-load of 1 N at the crosshead speed of 1 mm/min and a 10 mm span between supports.

### 2.4.3 TGA tests

The determination of mass fractions of composites made from carbon fibre and polymer with high temperature resistance like Primospire® is difficult and usually assessed by image processing techniques. Standard calcination tests are the mostly used with glass-reinforced plastics composites.

In this work we intend to use calcination tests for the evaluation of fibre mass fraction on carbon fibre and Primospire® composites, but since there's only a partial degradation of reinforcement and matrix, this method cannot be applied directly as in the case of glass-reinforced plastics composites.

In order to obtain carbon fibre and Primospire® temperature degradation behaviour TGA test were carried out using a thermo-gravimetric balance TA Q500 under different atmospheres (inert, oxidative and air).

In tests made under inert ($N_2$), oxidative ($O_2$) and air atmospheres, carbon fibres and polymer samples were heated from 30/40/60ºC until 900ºC using a 10ºC/min constant heating rate.

Being Air the atmosphere in the muffle furnace for calcination, TGA tests were also carried out under the same condition.

Polypropylene polymer matrix was also submitted to TGA tests with air as atmosphere to evaluate its degradation behaviour which is a relevant parameter to the determination of the processing conditions of composites that uses this polymer.

To avoid weight loss due to air flow, this was not used in all TGA tests performed with air atmosphere.

### 2.4.4 Calcination testing

Calcination tests were carried on the CF/Primospire® composites using results obtained from the TGA tests since this polymer matrix exhibits high temperature resistance and so is not fully eliminated on conventional calcination tests.

Initially, matrix (Primospire®) and reinforcement (CF) mass loss curves as a function of time resulting from the TGA tests were evaluated. This analysis concluded that the temperature 700 ºC was a good compromise between the end of Primospire® high degradation rate and the beginning of significant carbon fibre mass loss.

In order to simulate TGA behaviour calcination tests were performed on the constituents of the studied composite using the same thermal cycle (10° C/min) until the temperature of 700 ºC was reached. The initial mass of the samples, placed in a ceramic crucible, was approximately 2 g in accordance with the conventional standard.

CF/PP composites fibre mass content was determined by using calcination tests according to the EN ISO 1172. Composite samples, weighting approximately 2 g, were submitted to calcination inside a crucible in a muffle furnace during 10 min at 625º C.

## 3. Results and Discussion

The cross-sections of the pultruded composites were studied under optical Microscopy. As can be seen from Figures 4 and 5, all CF/PP and CF/Primospire® composite profiles from towpregs (with and without additive) and PCT´s have a reasonable distribution of the reinforcing fibres over the cross-sections. However, large differences in impregnation quality occur between the different samples that are likely to be related, directly, to the impregnation state of pre-impregnated materials used in pultrusion. It may be seen that the impregnation quality of the PCT composite samples is good, presenting almost all fibres completely surrounded (‘wet-out’) by the polymer. Only a few large dry spots were observed. This is most likely due to the good degree of impregnation already achieved in the PCT raw-material tape prior to the pultrusion step.

The samples from CF/PP towpreg with additive show a higher quantity of dry zones than the ones without additive. This could be due to some lack of compatibility between the fibre sizing and the used maleic anhydride coupling agent.

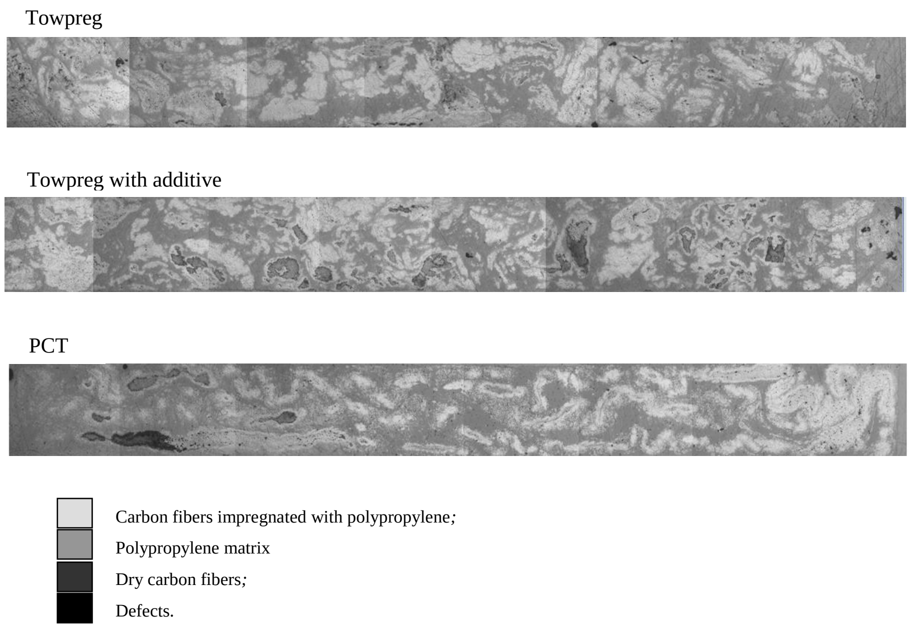


Figure 4. Optical micrographs of pultruded profiles cross-section (magnification of 8.75×)

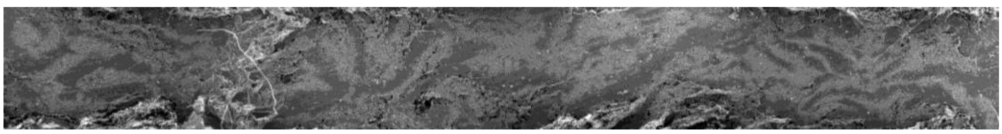

Figure 5. SEM image of CF/Primospire® pultruded profile cross-section sample (magnification of 40×)

Figure 6 show the results obtained in TGA test samples that were tested under inert and oxidative atmospheres. As can be seen, the polymer only shows the first degradation effects at temperatures above 450 ºC. It is also possible to conclude that, under inert atmosphere and until 900 ºC, only about 25% of the polymer mass is really lost. In the case of oxidative atmosphere almost all the polymer mass was completely lost at the final maximum temperature of 700 ºC.

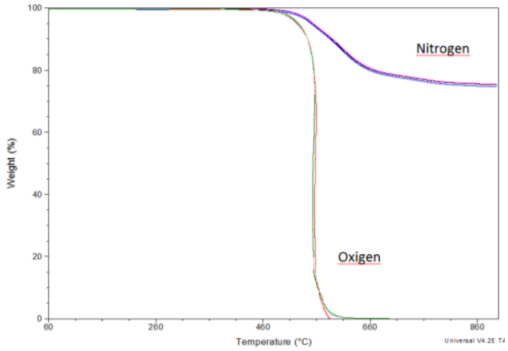


Figure 6. Comparison between the TGA results carried out on Primospire® under inert ($N_2$) and oxidative ($O_2$) atmospheres

The results obtained for carbon fibre and Primospire® TGA tests under air atmosphere (Figure 7) show that the degradation behaviour is between the one found for inert and oxidative atmospheres.

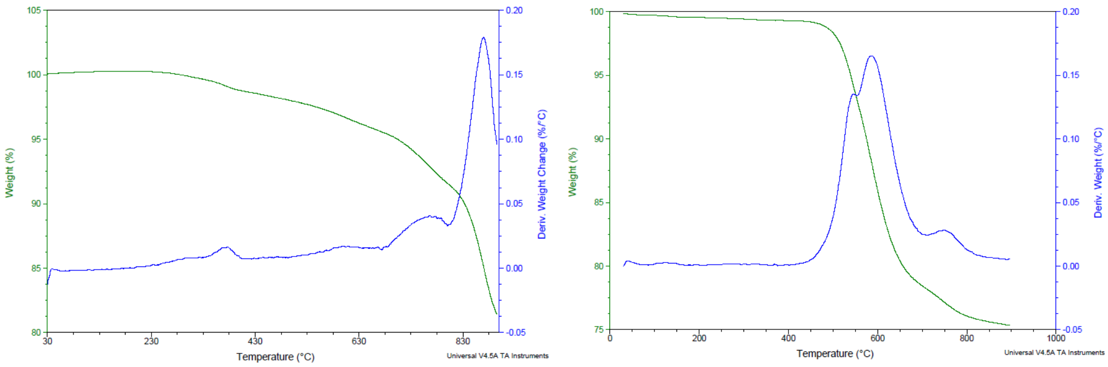


Figure 7. TGA results carried out on carbon fibres (left) and Primospire® (right) under air atmosphere

The results obtained in the calcination (Table 4) were similar to those of the TGA tests. The calcinations of Primospire® and carbon fibres at 700 ºC allowed establishing 25.9% and 7.2% as average mass losses, respectively, and as a consequence, the proportion of the remaining mass was 74.1% (wf) and 93.8% (wp). In TGA tests, the average mass loss of carbon fibre and Primospire® was 21.55% and 5.97%, respectively. Then, it was applied to the composite the same calcination parameters that were used for the testing of their constitutive materials.

| **Experiments** | **Loss mass** (%) | |
|---|---|---|
| | Primospire® | Carbon Fibre |
| 1 | 25.9 | 6.1 |
| 2 | 26.4 | 7.5 |
| 3 | 26.1 | 7.2 |
| 4 | 25.3 | 7.8 |
| Average | **25.9** | **7.2** |
| SD | 0.5 | 0.7 |
| Remaining mass fraction (w) | **74.1** | **93.8** |

Table 4. Primospire® and carbon fibre calcination results

After calcining the composite sample, the carbon fibre mass fraction, wfc, was obtained by:

$$wfc = 1 - \frac{mc_f - wf \cdot mc_i}{mc_i \cdot (wp - wf)} \qquad (1)$$

where $mc_i$ and $mc_f$ are the measured composite sample initial and final weights, respectively. Also, $wf$ and $wp$ are the carbon fibre and Primospire® remaining mass fractions, respectively.

Furthermore, by knowing the fiber and polymer densities, $\rho_f$ and $\rho_p$, respectively, the fiber mass fraction ($wfc$) may be converted in fiber volume fraction ($vf$) by:

$$vf = \frac{\frac{wfc}{\rho f}}{\frac{wfc}{\rho f} + \frac{(1 - wfc)}{\rho p}} \qquad (2)$$

Table 5 summarizes the composite calcination test obtained results. As can be seen, the composite had a fibre mass fraction of 54.1% corresponding to a fibre volume fraction of 45.2%.

| **Experiments** | **Loss mass** (%) | **Fibre mass fraction** (wfc) | **Fibre volume fraction** ($vf$) |
|---|---|---|---|
| 1 | 16.6 | 49.9 | 41.1 |
| 2 | 16.8 | 48.8 | 40.0 |
| 3 | 15.8 | 54.2 | 45.2 |
| 4 | 16.4 | 50.8 | 41.9 |
| 5 | 14.7 | 59.9 | 51.1 |
| 6 | 14.5 | 60.9 | 52.1 |
| Average | **15.8** | **54.1** | **45.2** |
| SD | 1.0 | 5.2 | 5.3 |

Table 5. Composite calcination test results

Concerning polypropylene TGA tests, it was found that the degradation temperature was about 270 ºC (Figure 8).

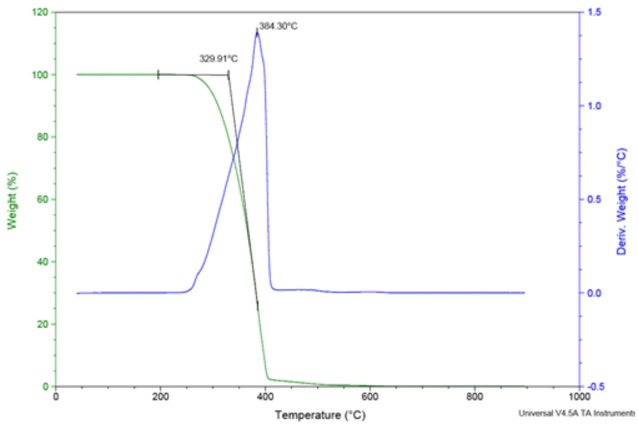


Figure 8. TGA results carried out on polypropylene under air atmosphere.

Tables 6 and 7 summarize all experimentally results obtained from the CF/PP and CF/Primospire® composites processed by pultrusion from the pre-impregnated products under study. To better evaluate and compare the mechanical properties obtained on the composites processed from the different pre-impregnated products studied. The tables also present theoretical expected values and relative values of specific properties.

As can be seen from Table 6 the experimental moduli obtained from de CF/PP composites are in good agreement with the predicted theoretical ones. Some experimental values are even higher than the theoretical expected ones. This can be explained considering that the volume fraction content of some samples can be higher than the determined by the calcination tests.

Analysing Table 6, one can conclude that composites processed from the CF/PP PCT´s demonstrated to have better flexural and interlaminar shear strengths than those produced from CF/PP towpregs. Concerning the interlaminar shear tests, the CF/Primospire® composites shown a much higher value than CF/PP probably due to the better mechanical properties that the Primospire® matrix exhibits. As it may be seen and expected, the CF/Primospire® towpregs required the use of much higher temperatures than the CF/PP ones in pre-heating furnace and pressurization/consolidation die. Due to such higher temperatures, tests still continue being done to optimise the operational conditions and, consequently, the obtained mechanical properties.

Finally, it may be noted that any of composites made from pre-impregnated materials under study reached failure in the interlaminar shear tests. This fact reveals the high degree of ductility exhibited by these materials which may be relevant for many applications. Thus, the interlaminar shear strength results shown in Tables 6 and 7 correspond to maximum force applied in the test.

| **Test Type** | **Property** | | ***Pultrusion*** | |
|---|---|---|---|---|
| | | | ***Towpreg*** | ***PCT*** |
| **Flexural** | Flexure Modulus (GPa) | Experimental | 90.1±0.4 | 37.7±2.2 |
| | | Theoretical | 98.9 | 62.7 |
| | Flexure Modulus / Fibre volume fraction (GPa) | | 178.1±0.8 | 118.2±6.9 |
| | Flexure Strength (MPa) | Experimental | 241.2±1.6 | 158.7±4.2 |
| | Flexure Strength / Fibre volume fraction (MPa) | | 476.7±3.2 | 497.5±13.2 |
| **Tensile** | Tensile Modulus (GPa) | Experimental | 110.6±5.9 | 63.5±4.3 |
| | | Theoretical | 98.9 | 62.7 |
| | Tensile Modulus / Fibre volume fraction (GPa) | | 218.6±11.7 | 199.1±13.5 |
| | Tensile Strength (MPa) | Experimental | 1060.8±43.1 | 636.9±38.4 |
| | Tensile Strength / Fibre volume fraction (MPa) | | 2096.4±85.2 | 1996.6±120.4 |
| **Inter-laminar Shear** | Interlaminar Shear Strength (MPa) | | 12.3±0.3 | 14.0±0.2 |
| Fibre volume fraction (%) | | | 50.6 | 31.9 |

Table 6. CF/PP composite mechanical test results

| ***Test Type*** | **Property** | **Pultrusion** |
|---|---|---|

| | | CF/Primospire® towpreg |
|---|---|---|
| **Flexural** | Flexure Modulus (GPa) | 56.1±2.9 |
| | Flexure Strength (MPa) | 253.6±16.1 |
| **Tensile** | Tensile Modulus (GPa) | 92.2±5.6 |
| | Tensile Strength (MPa) | 839.2±28.7 |
| **Inter-laminar Shear** | Interlaminar Shear Strength (MPa) | 25.4±2.1 |

Table 7. Test results on the processed CF/Primospire® composites

The theoretical values of moduli, E, were directly obtained from the rule of mixtures using the raw-material properties presented in Tables 1 and 2, following the Eq. 3:

$$E = E_f \cdot vf + E_p \cdot (1 - vf) \qquad (3)$$

where, *Ef*, *Ep* and *vf* are the fibre modulus, polymer modulus and fibre volume fraction, respectively.

In the case of CF/Primospire® composites, using expression 3 and the experimental tensile moduli, it was possible to estimate the fibre volume fraction as approximately 45%. This result is in good agreement whit the one obtained from calcination test (45.2±5.3).

## 4. Conclusions

The tests made using a proprietary pultrusion equipment already allow to conclude that is possible to produce, in good conditions, profiles from almost all available thermoplastic matrix pre-impregnated raw-materials using pull speeds of 0.3 m/min.

Existing powder-coating equipment was shown to be suitable to produce CF/PP and CF/Primospire® towpregs that could be adequately processed into pultruded profiles. From the tests made, the towpregs can be easily and continuously produced at industrial production speeds between 2 a 8 m/min.

It was possible to optimize the production of CF/PP pultruded profiles and CF/PP towpregs, through the use of Taguchi/DOE method, achieving optimal conditions.

In particular, for CF/PP pultruded profiles, very good agreement was found between the experimental moduli values of all composites produced and the theoretical ones.

More research must be done in order to increase the processing speeds of CF/PP and CF/Primospire® towpregs as well as PCT's and to improve the impregnation, uniformity and dispersion of raw-materials in the composites.

CF/Primospire® composites obtained by pultrusion showed a higher value for the interlaminar strength than all other ones. Due to higher processing temperatures, further tests should be done to optimise the operational conditions and further improve the obtained composite mechanical properties.

The mechanical properties obtained in all pultruded composites allow predicting their adequate use either in general or structural engineering applications.

The calcination tests based on the results obtained from TGA tests reveal to be a very interesting method to experimentally determine composite mass fractions in the case of temperature resistant materials used as matrix and reinforcement.

Primospire® TGA tests showed that this material exhibits an excellent temperature resistance and, therefore, is a good candidate for high-demanding applications.

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